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FOR: LITHIUM-COBALT COMPOSITE OXIDE, PROCESS FOR ITS PRODUCTION, POSITIVE ELECTRODE FOR LITHIUM SECONDARY CELL EMPLOYING IT, AND LITHIUM SECONDARY CELL

DECLARATION

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SIR:

Now comes MASAYUKI KUWANO who deposes and says:

That my name is MASAYUKI KUWANO ;

That my address is 5-24-310, 3-chome, Nakacho, Musashino-shi, Tokyo, Japan;

That I know well both the English and Japanese languages;

That the attached English language translation is true and correct translation of Japanese Patent Application No. JP11-287781 filed on October 8, 1999 to the best of my knowledge and belief;

I hereby declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

FURTHER DEPONENT SAITH NOT.

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Date

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【TITLE OF THE INVENTION】

LITHIUM-COBALT COMPOSITE OXIDE AND PROCESS FOR ITS  
PRODUCTION

5 【SCOPE OF THE CLAIM(S)】

【Claim 1】

A hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which is represented by the formula  $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$ , wherein  $x$  is  $0.0005 \leq x \leq 0.02$  and M is at least one member selected from the group consisting of Ta, Ti and Nb, and which has a half-width of the diffraction peak for (110) face at  $2\theta = 66.5 \pm 1^\circ$ , of from 0.080 to  $0.180^\circ$ , as measured by the X-ray diffraction using  $\text{CuK}_\alpha$  as a ray source.

15 【Claim 2】

The hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, wherein  $x$  is  $0.001 \leq x \leq 0.01$ , and the half-width of the diffraction peak for (110) face is from  $0.100$  to  $0.165^\circ$ .

20 【Claim 3】

A process for producing the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in Claim 1 or 2, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to 20  $\mu\text{m}$  and a specific surface area of from 2 to 200  $\text{m}^2/\text{g}$ , a lithium carbonate powder having an average

particle size of from 1 to 50  $\mu\text{m}$  and a specific surface area of from 0.1 to 10  $\text{m}^2/\text{g}$ , and a powder of an oxide of metal element M having an average particle size of at most 5  $\mu\text{m}$  and a specific surface area of from 1 to 100  $\text{m}^2/\text{g}$ , and firing the mixture at a temperature of from 850 to 950°C in an oxygen-containing atmosphere for from 4 to 30 hours.

**[DETAILED DESCRIPTION OF THE INVENTION]**

**[Technical Field to which the Invention Belongs]**

10 The present invention relates to an improved lithium-cobalt composite oxide for a lithium secondary cell, and a process for its production.

**[Prior Art]**

In recent years, along with the progress in portable  
15 or codeless equipments, a demand is mounting for a non-aqueous electrolyte secondary cell which is small in size and light in weight and has a high energy density. As an active material for a non-aqueous electrolyte secondary cell, a composite oxide of lithium and a transition metal, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ,  $\text{LiMn}_2\text{O}_4$  or  $\text{LiMnO}_2$ , has been known.

Especially, a lithium secondary cell employing a lithium-cobalt composite oxide ( $\text{LiCoO}_2$ ) as a positive electrode active material and employing a lithium alloy  
25 or a carbon such as graphite or carbon fiber as a negative electrode, provides a high voltage at a level of 4 V and is widely used as a cell having a high energy

density.

However, a non-aqueous electrolyte secondary cell using LiCoO<sub>2</sub> as a positive electrode active material has had a problem of deterioration of the cycle characteristics such that the cell discharge capacity gradually decreases as a charge/discharge cycle is repeated, or a problem that the reduction of the discharge capacity is substantial at a low temperature.

In order to improve such cell properties, JP-A-7-32017 proposes to use as a positive electrode active material LiCoO<sub>2</sub> having from 5 to 35% of Co atoms replaced with W, Mn, Ta, Ti or Nb, for improvement of the cycle characteristics. Further, JP-A-6-64928 proposes to improve the self-discharge characteristics of a lithium secondary cell by using a Ti-containing lithium-cobalt composite oxide prepared by a synthesis employing a molten salt.

Further, JP-A-10-1316 proposes to use as an active material which is obtained by dispersing in an aqueous lithium hydroxide solution e.g. cobalt hydroxide or cobalt oxyhydroxide wherein the valence of cobalt is trivalent, followed by heat treatment, for the purpose of improving the cycle characteristics, etc. Further, JP-A-10-279315 proposes to obtain an active material having a high capacity and good cycle characteristics by firing e.g. dicobalt trioxide (Co<sub>3</sub>O<sub>2</sub>) or cobalt oxyhydroxide wherein the valence of cobalt is trivalent, with e.g.

lithium oxide at a temperature of from 250 to 1,000°C.

Further, JP-A-10-312805 proposes to improve the cycle characteristics by using as a positive electrode active material LiCoO<sub>2</sub> of a hexagonal system having a crystallite diameter of from 45 to 100 nm in a (110) direction of the crystallite, wherein the length of c axis of lattice constant is at most 14.051 Å.

**【Problems that the Invention is to Solve】**

However, with respect to a lithium secondary cell using LiCoO<sub>2</sub> as a positive electrode active material, no product has been known which fully satisfies all of requirements for cycle characteristics, the initial capacity, and the low temperature operation efficiency, and for a production method for efficient mass production.

It is an object of the present invention to provide a positive electrode active material for a lithium secondary cell which has a large electric capacity and good discharge characteristics at low temperatures, is excellent in the charge/discharge cycle durability, and has high safety, and a process for its production.

**【Means of Solving the Problems】**

The present inventors have found that an active material having a specific composition and crystal structure, is excellent in the cell properties, and particularly, an active material obtained by a specific production process is especially excellent in cycle

characteristics, low temperature operation efficiency, and mass productivity.

The present invention provides a hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which is represented by the formula  $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$ , wherein  $x$  is  $0.0005 \leq x \leq 0.02$  and  $M$  is at least one member selected from the group consisting of Ta, Ti and Nb, and which has a half-width of the diffraction peak for (110) face at  $2\theta = 66.5 \pm 1^\circ$ , of from  $0.080$  to  $0.180^\circ$ , as measured by the X-ray diffraction using  $\text{CuK}_\alpha$  as a ray source.

If  $x$  is smaller than  $0.0005$ , the effects for improving the cycle durability and low temperature operation efficiency decrease, such being undesirable. If  $x$  is larger than  $0.02$ , the initial electric capacity decreases, such being undesirable.  $x$  is preferably  $0.001 \leq x \leq 0.01$ , particularly preferably  $0.002 \leq x \leq 0.007$ .

The half-width of the diffraction peak for (110) face at  $2\theta = 66.5 \pm 1^\circ$ , as measured by the X-ray diffraction using  $\text{CuK}_\alpha$  as a ray source, reflects the crystallite diameter in a certain specific direction of a lithium-containing composite oxide, and a relation has been found such that the larger the half width of the peak, the smaller the crystallite diameter. In the present invention, the half-width of the peak means the width of the peak at  $1/2$  of the height of the peak.

The half-width of the diffraction peak for (110) face of the present invention is from  $0.080$  to  $0.180^\circ$ .

- If such a half-width is less than 0.080°, the charge/discharge cycle durability, initial electric capacity, average discharge voltage or safety of the cell employing it as a positive electrode active material,
- 5 tends to deteriorate, such being undesirable. If such a half-width exceeds 0.180°, the initial electric capacity and safety of the cell tend to be low, such being undesirable. The particularly preferred range is from 0.100 to 0.165°.
- 10 Further, the present invention provides a process for producing a hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to 20 µm and a specific surface area of from 2 to 200 m<sup>2</sup>/g, a lithium carbonate powder having an average particle size of from 1 to 50 µm and a specific surface area of from 0.1 to 10 m<sup>2</sup>/g, and a powder of an oxide of metal element M having an average particle size of at most 5 µm and a specific surface area
- 15 of from 1 to 200 m<sup>2</sup>/g, which may be added as the case requires, followed by firing from 850 to 950°C in an oxygen-containing atmosphere for from 4 to 30 hours.
- 20

In the present invention, the average particle size means a weight average particle diameter. In the present invention, the average particle size is a particle size at a point where the cumulative curve of mass becomes 50% in the cumulative curve for the total mass of 100%

prepared by obtaining the particle size distribution based on mass. This may be referred to also as a mass base cumulative 50% diameter (for example, Chemical Engineering Handbook "Fifth Edition" (compiled by 5 Chemical Engineering Association) p 220-221. The measurement of the particle size is carried out by thoroughly dispersing in a medium such as water by means of e.g. ultrasonic treatment and measuring the particle size distribution (for example, by using Microtruck HRAX-10 100, manufactured by Nikkiso co., Ltd.).

For the process of the present invention, cobalt oxyhydroxide of specific properties is used as a cobalt material. If the average particle size of the cobalt oxyhydroxide is less than 1  $\mu\text{m}$ , the safety of the cell 15 tends to decrease, or the packing density of the positive electrode layer tends to decrease, whereby the electrical capacity per volume tends to decrease, such being undesirable. Further, if the average particle size of the cobalt oxyhydroxide exceeds 20  $\mu\text{m}$ , the discharge 20 characteristics of the cell at a large current tend to decrease, such being undesirable. A preferred average particle size of the cobalt oxyhydroxide is from 4 to 15  $\mu\text{m}$ . The cobalt oxyhydroxide may sometimes be produced in a hydrous state. In such a case, the specific surface 25 area can hardly be measured. Accordingly, in the present invention, the specific surface area of hydrous cobalt oxyhydroxide means the specific surface area with respect

to a powder obtained by drying the hydrate of cobalt oxyhydroxide at 120°C for 16 hours for dehydration.

Further, when hydrous cobalt oxyhydroxide is to be used, it is preferred to use a powder after drying it.

- 5 For example, it is preferred to employ it after drying at 120°C for 16 hours. In the present invention, if the specific surface area of the cobalt oxyhydroxide is less than 2 m<sup>2</sup>/g, the discharge capacity at a large current tends to decrease, such being undesirable. Further, if  
10 the specific surface area of the cobalt oxyhydroxide exceeds 200 m<sup>2</sup>/g, the packing density of the positive electrode layer tends to decrease, whereby the electric capacity per volume tends to decrease, such being undesirable. A preferred specific surface area of the  
15 cobalt oxyhydroxide is from 20 to 100 m<sup>2</sup>/g.

For the process of the present invention, lithium carbonate having a specific nature is used as a lithium material. If the average particle size of the lithium carbonate is less than 1 μm, the bulk density of the  
20 powder tends to decrease, and the productivity in mass production tends to decrease, such being undesirable. Further, if the average particle size of the lithium carbonate exceeds 100 μm, the initial electric capacity tends to decrease, such being undesirable. A  
25 particularly preferred average particle size of the lithium carbonate is from 5 to 30 μm. If the specific surface area of the lithium carbonate is less than 0.1

$\text{m}^2/\text{g}$ , the initial discharge capacity per unit weight tends to decrease, such being undesirable. Further, if the specific surface area of the lithium carbonate exceeds  $10 \text{ m}^2/\text{g}$ , the packing density of the positive electrode layer tends to decrease, whereby the electric capacity per volume tends to decrease, such being undesirable. A particularly preferred specific surface area of the lithium carbonate is from 0.3 to  $3 \text{ m}^2/\text{g}$ .

In the present invention, a metal oxide having a specific nature is used as a metal oxide containing metal element M, as a raw material. The metal oxide containing metal element M may be titanium oxide  $\text{TiO}_2$  when M is titanium (Ti). Titanium oxide includes an anatase type, a rutile type, etc. It is particularly preferred to use an anatase type, since the cell properties will be good. When M is niobium (Nb),  $\text{Nb}_2\text{O}_5$  may be mentioned. When M is tantalum (Ta),  $\text{Ta}_2\text{O}_5$  may be mentioned.

If the average particle size of the metal oxide exceeds  $5 \mu\text{m}$ , the distribution of metal element M in the positive electrode active material particles tends to be non-uniform, whereby the effects of adding element M relating to the cell performance tend to decrease, such being undesirable. A preferred average particle size of the oxide of metal element M is at most  $1 \mu\text{m}$ , particularly preferably at most  $0.3 \mu\text{m}$ .

If the specific surface area of the metal oxide containing metal element M is less than  $1 \text{ m}^2/\text{g}$ , the

reactivity tends to decrease, whereby the effects of adding metal element M relating to the cell performance tend to decrease, such being undesirable. On the other hand, if the specific surface area of the metal oxide containing element M exceeds 100 m<sup>2</sup>/g, element M tends to be uniformly incorporated into the crystal lattice, whereby the effects of adding metal element M relating to the cell performance tend to decrease, such being undesirable. A preferred specific surface area of the oxide of metal element M is from 2 to 20 m<sup>2</sup>/g.

The lithium-cobalt composite oxide of the present invention is obtained by dry blending the cobalt oxyhydroxide powder, the lithium carbonate powder and the oxide powder containing metal element M, followed by firing from 850 to 950°C for from 4 to 30 hours in an oxygen-containing atmosphere. Wet blending is not preferred, since the productivity is low. If the firing temperature is lower than 850°C, the charge/discharge cycle durability tends to be low, such being undesirable. On the other hand, if the firing temperature exceeds 950°C, the initial electric capacity tends to decrease, such being undesirable. Particularly preferred is from 880 to 920°C. If the firing time is less than 4 hours, the firing state tends to be non-uniform during mass production, whereby fluctuation is likely to result in the properties, such being undesirable. If it exceeds 30 hours, the productivity tends to decrease, such being

undesirable. It is particularly preferred to employ a firing time of from 8 to 20 hours.

The firing of the above mixture is carried out preferably in an oxygen stream. The oxygen concentration 5 in the stream is preferably from 10 to 100 volume%, particularly preferably from 19 to 50 volume%. If the oxygen concentration is low, the cell performance tends to deteriorate, such being undesirable. The positive electrode active material obtained by the process of the 10 present invention and having the specific value of the half-width of the diffraction peak for (110) face, has a higher low temperature operation efficiency than ever, and is excellent in the charge/discharge cycle durability, while maintaining the initial electric 15 capacity.

A positive electrode composite material is obtained by mixing a binder with an electrically conductive material, a carbon type conductive material such as acetylene black, graphite or ketjenblack, is, for 20 example, preferably employed. As the binder, polyvinylidene fluoride, polytetrafluoroethylene, polyamide, carboxymethyl cellulose or an acrylic resin may, for example, be employed.

In the present invention, a kneaded product or a 25 slurry comprising the powder of the composite oxide of the present invention, an electrically conductive material, a binder and a solvent or dispersant for the

binder, is coated on a positive electrode current collector made of e.g. an aluminum foil or a stainless steel foil to have it supported on the current collector to obtain a positive electrode plate. As the separator, 5 a porous polyethylene film or a porous polypropylene film may, for example, be employed.

In the lithium secondary cell using the positive electrode active material of the present invention, as the solvent for the electrolyte solution, a carbonic 10 ester is preferred. The carbonic ester may be cyclic or chain. The cyclic carbonic ester may, for example, be propylene carbonate or ethylene carbonate (EC). The chain carbonic ester may, for example, be dimethyl carbonate, diethyl carbonate (DEC), ethylmethyl 15 carbonate, methylpropyl carbonate or methylisopropyl carbonate.

In the present invention, the above carbonic esters may be used alone or in combination as a mixture of two or more of them. Further, such an ester may be mixed 20 with other solvent. Further, depending upon the material for the negative electrode active material, there may be a case where the charge/discharge characteristics, cycle durability or charge/discharge efficiency can be improved by a combined use of a chain carbonic ester and a cyclic 25 carbonic ester.

Further, to such an organic solvent, a vinylidene fluoride/hexafluoropropylene copolymer (for example,

Keiner, tradename, manufactured by Atochem Company) and vinylidene fluoride/perfluoropropyl vinyl ether copolymer disclosed in JP-A-10-294131, may be added, and the following solute may be added to obtain a gel polymer 5 electrolyte.

As the solute, it is preferred to use at least one member of lithium salts containing e.g.  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{CF}_3\text{CO}_2^-$  or  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  as an anion. For the above electrolyte solution or polymer 10 electrolyte, it is preferred to add the electrolyte made of a lithium salt to the above solvent or solvent-containing polymer at a concentration of from 0.2 to 2.0 mol/l. If the concentration departs from this range, the ion conductivity tends to decrease, and the electrical 15 conductivity of the electrolyte tends to decrease. The concentration is more preferably adjusted to be from 0.5 to 1.5 mol/l.

In the lithium secondary cell employing a positive electrode active material of the present invention, as 20 the negative electrode active material, a material capable of absorbing and desorbing lithium ions, is employed. The material for such a negative electrode active material is not particularly limited, but, it may, for example, be a lithium metal, a lithium alloy, a 25 carbon material, an oxide composed mainly of a metal of Group 14 or 15 of the Periodic Table, a carbon compound, a silicon carbide compound, a silicon oxide compound,

titanium sulfide or a boron carbide compound. As the carbon material, one obtained by thermally decomposing an organic material by various thermal decomposition conditions, or artificial graphite, natural graphite, 5 soil graphite, expanded graphite or scaly graphite, may, for example, be used. Further, as the oxide, a compound composed mainly of tin oxide, may be used. As the negative electrode current collector, a copper foil or a nickel foil may, for example, be used.

10 The positive electrode and the negative electrode in the present invention are obtained preferably by kneading the active material with an organic solvent to obtain a slurry, and coating the slurry on a metal foil current collector, followed by drying and pressing. There is no 15 particular restriction as to the shape of the lithium secondary cell of the present invention. A sheet shape (so-called film shape), folded-shape, wounded bottomed cylindrical shape or a button shape, may suitably be selected depending upon the particular application.

20 **[Examples]**

Now, the present invention will be described in further detail with reference to Examples, but it should be understood that the present invention is by no means restricted to such Examples.

25 **EXAMPLE 1**

A cobalt oxyhydroxide powder having an average particle size of 10  $\mu\text{m}$  and a specific surface area of 66

$\text{m}^2/\text{g}$ , a lithium carbonate powder having an average particle size of 15  $\mu\text{m}$  and a specific surface area of 1.2  $\text{m}^2/\text{g}$  and an anatase-type titanium dioxide powder having an average particle size of 0.22  $\mu\text{m}$  and a specific surface area of 9  $\text{m}^2/\text{g}$ , were mixed. The mixing ratio was such that the composition would be  $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$  after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the X-ray diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using  $\text{CuK}_\alpha$  ray, the half-width of the diffraction peak for (110) face in the vicinity of  $2\theta = 66.5 \pm 1^\circ$ , was  $0.121^\circ$ .

The  $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$  powder thus obtained, acetylene black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and kneaded while adding toluene, followed by drying to obtain a positive electrode plate having a thickness of 150  $\mu\text{m}$ .

And, two stainless steel simple closed cells were assembled in an argon glove box, by using an aluminum foil having a thickness of 20  $\mu\text{m}$  as a positive electrode current collector, using a porous polypropylene film having a thickness of 25  $\mu\text{m}$  as a separator, using a metal

lithium foil having a thickness of 500  $\mu\text{m}$  as a negative electrode, using a nickel foil of 20  $\mu\text{m}$  as a negative electrode current collector, and using 1M LiPF<sub>6</sub>/EC+DEC (1:1) as an electrolyte.

5       With respect to these two cells, firstly, charging was carried out to 4.3 V at a load current of 75 mA per g of the positive electrode active material at 25°C, and discharging was carried out to 2.5 V at an applied current of 75 mA per g of the positive electrode active  
10 material, whereby the initial discharge capacity was obtained. With respect to one cell, the charge/discharge cycle test was further carried out 40 times. Further, the other cell was charged at 25°C and then cooled to -10°C. Then, discharging was carried out to 2.5 V by a  
15 load current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity at -10°C was obtained, and the capacity development rate at -10°C was obtained, on the basis that the initial electric capacity at 25°C was 100%.

20       The initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.3%. Further, the capacity developing rate at -10°C was 70%.

#### EXAMPLE 2

25       A cobalt oxyhydroxide powder having an average particle size of 10  $\mu\text{m}$  and a specific surface area of 66  $\text{m}^2/\text{g}$ , a lithium carbonate powder having an average

particle size of 15  $\mu\text{m}$  and a specific surface area of 1.2  $\text{m}^2/\text{g}$  and a niobium oxide  $\text{Nb}_2\text{O}_5$  powder having an average particle size of 0.15  $\mu\text{m}$  and a specific surface area of 5.3  $\text{m}^2/\text{g}$ , were mixed. The mixing ratio was such that the  
5 composition would be  $\text{LiCo}_{0.998}\text{Nb}_{0.002}\text{O}_2$  after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

10 With respect to the powder after the firing (the positive electrode active material powder), the X-ray diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using  $\text{CuK}\alpha$  ray, the half-width of the diffraction peak for (110) face in the vicinity of  $2\theta = 66.5 \pm 1^\circ$ , was  $0.115^\circ$ .  
15

The  $\text{LiCo}_{0.998}\text{Nb}_{0.002}\text{O}_2$  powder thus obtained, acetylene black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and kneaded while adding  
20 toluene, followed by drying to obtain a positive electrode plate having a thickness of 150  $\mu\text{m}$ .

And, two stainless steel simple closed cells were assembled in an argon grove box, by using an aluminum foil having a thickness of 20  $\mu\text{m}$  as a positive electrode  
25 current collector, using a porous polypropylene film having a thickness of 25  $\mu\text{m}$  as a separator, using a metal lithium foil having a thickness of 500  $\mu\text{m}$  as a negative

electrode, using a nickel foil of 20  $\mu\text{m}$  as a negative electrode current collector, and using 1M LiPF<sub>6</sub>/EC+DEC (1:1) as an electrolyte.

With respect to these two cells, firstly, charging 5 was carried out to 4.3 V at a load current of 75 mA per g of the positive electrode active material at 25°C, and discharging was carried out to 2.5 V at an applied current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity was 10 obtained. With respect to one cell, the charge/discharge cycle test was further carried out 40 times. Further, the other cell was charged at 25°C and then cooled to -10°C. Then, discharging was carried out to 2.5 V by a load current of 75 mA per g of the positive electrode 15 active material, whereby the initial discharge capacity at -10°C was obtained, and the capacity development rate at -10°C was obtained, on the basis that the initial electric capacity at 25°C was 100%.

The initial discharge capacity at from 2.5 to 4.3 V 20 at 25°C was 148 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.0%. Further, the capacity developing rate at -10°C was 73%.

#### EXAMPLE 3

A cobalt oxyhydroxide powder having an average 25 particle size of 10  $\mu\text{m}$  and a specific surface area of 66  $\text{m}^2/\text{g}$ , a lithium carbonate powder having an average particle size of 15  $\mu\text{m}$  and a specific surface area of 1.2

$\text{m}^2/\text{g}$  and a tantalum oxide  $\text{Ta}_2\text{O}_5$  powder having an average particle size of  $0.23 \mu\text{m}$  and a specific surface area of  $9.8 \text{ m}^2/\text{g}$ , were mixed. The mixing ratio was such that the composition would be  $\text{LiCo}_{0.998}\text{Ta}_{0.002}\text{O}_2$  after firing. These 5 three types of powders were dry-blended and then fired at  $910^\circ\text{C}$  for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the 10 positive electrode active material powder), the X-ray diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using  $\text{CuK}_\alpha$  ray, the half-width of the diffraction peak for (110) 15 face in the vicinity of  $2\theta = 66.5 \pm 1^\circ$ , was  $0.115^\circ$ .

The  $\text{LiCo}_{0.998}\text{Ta}_{0.002}\text{O}_2$  powder thus obtained, acetylene black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and kneaded while adding toluene, followed by drying to obtain a positive 20 electrode plate having a thickness of  $150 \mu\text{m}$ .

And, two stainless steel simple closed cells were assembled in an argon grove box, by using an aluminum foil having a thickness of  $20 \mu\text{m}$  as a positive electrode current collector, using a porous polypropylene film 25 having a thickness of  $25 \mu\text{m}$  as a separator, using a metal lithium foil having a thickness of  $500 \mu\text{m}$  as a negative electrode, using a nickel foil of  $20 \mu\text{m}$  as a negative

electrode current collector, and using 1M LiPF<sub>6</sub>/EC+DEC (1:1) as an electrolyte.

With respect to these two cells, firstly, charging was carried out to 4.3 V at a load current of 75 mA per g of the positive electrode active material at 25°C, and discharging was carried out to 2.5 V at an applied current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity was obtained. With respect to one cell, the charge/discharge cycle test was further carried out 40 times. Further, the other cell was charged at 25°C and then cooled to -10°C. Then, discharging was carried out to 2.5 V by a load current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity at -10°C was obtained, and the capacity development rate at -10°C was obtained, on the basis that the initial electric capacity at 25°C was 100%.

The initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 20 40 charge/discharge cycles, was 96.1%. Further, the capacity developing rate at -10°C was 75%.

#### EXAMPLE 4

A cobalt oxyhydroxide powder having an average particle size of 8 µm and a specific surface area of 40 m<sup>2</sup>/g, a lithium carbonate powder having an average particle size of 22 µm and a specific surface area of 0.64 m<sup>2</sup>/g and an anatase-type titanium dioxide powder

having an average particle size of 0.17  $\mu\text{m}$  and a specific surface area of  $35 \text{ m}^2/\text{g}$ , were mixed. The mixing ratio was such that the composition would be  $\text{LiCo}_{0.994}\text{Ti}_{0.006}\text{O}_2$  after firing. These three types of powders were dry-blended and then fired at  $890^\circ\text{C}$  for 15 hours in an atmosphere having the oxygen concentration adjusted to 19 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the X-ray diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using  $\text{CuK}_\alpha$  ray, the half-width of the diffraction peak for (110) face in the vicinity of  $2\theta = 66.5 \pm 1^\circ$ , was  $0.127^\circ$ .

The  $\text{LiCo}_{0.994}\text{Ti}_{0.006}\text{O}_2$  powder thus obtained, acetylene black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and kneaded while adding toluene, followed by drying to obtain a positive electrode plate having a thickness of 150  $\mu\text{m}$ .

And, two stainless steel simple closed cells were assembled in an argon grove box, by using an aluminum foil having a thickness of 20  $\mu\text{m}$  as a positive electrode current collector, using a porous polypropylene film having a thickness of 25  $\mu\text{m}$  as a separator, using a metal lithium foil having a thickness of 500  $\mu\text{m}$  as a negative electrode, using a nickel foil of 20  $\mu\text{m}$  as a negative electrode current collector, and using 1M  $\text{LiPF}_6/\text{EC+DEC}$

(1:1) as an electrolyte.

With respect to these two cells, firstly, charging was carried out to 4.3 V at a load current of 75 mA per g of the positive electrode active material at 25°C, and 5 discharging was carried out to 2.5 V at an applied current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity was obtained. With respect to one cell, the charge/discharge cycle test was further carried out 40 times. Further, 10 the other cell was charged at 25°C and then cooled to -10°C. Then, discharging was carried out to 2.5 V by a load current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity at -10°C was obtained, and the capacity development rate 15 at -10°C was obtained, on the basis that the initial electric capacity at 25°C was 100%.

The initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.7%. Further, the 20 capacity developing rate at -10°C was 72%.

#### COMPARATIVE EXAMPLE 1

A positive electrode active material was synthesized in the same manner as in Example 1 except that no titanium oxide was added. The half-width of the 25 diffraction peak for (110) face measured in the same manner as in Example 1, was 0.098°. The measurement of the cell performance was carried out in the same manner

as in Example 1, whereby the initial electric capacity at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 94.8%. Further, the capacity developing rate at -10°C was 54%.

5 COMPARATIVE EXAMPLE 2

A positive electrode active material was synthesized in the same manner as in Example 1 except that the added amount of the titanium oxide was changed so that the composition would be  $\text{LiCo}_{0.95}\text{Ti}_{0.05}\text{O}_2$  after firing. The 10 half-width of the diffraction peak for (110) face measured in the same manner as in Example 1, was 0.188°. The measurement of the cell performance was carried out in the same manner as in Example 1, whereby the initial discharge capacity at 25°C was 141 mAh/g, and the 15 capacity retention after 40 charge/discharge cycles, was 93.6%. Further, the capacity developing rate at -10°C was 68%.

**[Effects of the Invention]**

According to the present invention, a positive 20 electrode active material for a lithium secondary cell which has a large electric capacity, good low temperature discharge characteristics, excellent charge/discharge cycle durability and high safety, will be provided.



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**[TYPE OF DOCUMENT]**

ABSTRACT

**[SUMMARY]**

**[OBJECT]**

A composite oxide suitable for a non-aqueous  
5 electrolyte secondary cell which can be used in a wide  
range of voltage, has a large electric capacity and  
excellent low temperature performance and is excellent in  
the durability for charge-discharge cycles and highly  
safe, is presented.

10 **[MEANS OF SOLVING PROBLEMS]**

The composite oxide is a hexagonal lithium-cobalt  
composite oxide for a lithium secondary battery, which is  
represented by the formula  $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$ , (wherein  $0.0005 \leq x \leq$   
0.02 and M is at least one member selected from the group  
15 consisting of Ta, Ti and Nb), and which has a half-width  
of the diffraction peak for (110) face at  $2\theta = 66.5 \pm 1^\circ$ , of  
from 0.080 to 0.180°, as measured by the X-ray  
diffraction using  $\text{CuK}_\alpha$  as a ray source.

**[SELECTED FIGURE]** No Selected Figure